Using Temperature Effects on Polymer-Composite Sensor Arrays to Identify Analytes

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Abstract

The sensor response of six different polymer-carbon-black composite sensors to three different analytes has been investigated as a function of temperature where the temperature range is 28-36 °C (ΔT is 4-8 °C). We tested the response of these polymer-carbon-black sensors to water, methanol and methane from 28-36 °C. All of the sensors showed a decrease in response to an analyte with increasing temperature; however, each sensor's response changes differently with temperature. This variation of response to temperature change creates distinct temperature-dependent fingerprints and will be useful in extending the range of data available for analyte identification and quantification.

Keywords

polymer-composite, sensor, temperature, Electronic Nose

INTRODUCTION

A miniature electronic nose (ENose) has been designed and built at the Jet Propulsion Laboratory; this ENose was designed to detect, identify and quantify ten common contaminants and relative humidity changes while monitoring air quality in an enclosed environment[1-4]. In this first generation array of sensors, polymer-carbon black composite films were used as the sensing films and the sensors were held at a constant temperature, 2-4 °C above ambient. The selection of the polymer-carbon black sensors was optimized for a targeted list of compounds. This array selection works well for identifying single analytes and mixtures of two and sometimes three analytes.

In order to extract the resistance response pattern, for the array, from raw time-series resistance data we process the data in several steps. The exact method of extracting the response pattern has been described elsewhere [1-4], but in general it involves three sequential steps: noise removal, baseline drifting accommodation, and relative resistance change calculation. It is the relative resistance changes across the array that become the fingerprint for an analyte.

The response of a sensor array may be enhanced or compromised by several factors including environmental condition such as pressure, humidity, and temperature. In some practical applications, changes due to temperature and humidity could be so large they could overshadow the fingerprints generated by the sensor array. This problem is often specifically treated in the data analysis of the array [4-6].

Sensor temperature effect studies have focused primarily on metal oxide sensors where a wide temperature range variation is possible (~70-450°C). [7, 8] The wide operating temperature range of the metal oxide sensors is attributed to its known thermal stability. Compared to the metal oxide sensors, polymer composite sensors operate over a small temperature range. This is primarily due to thermal stability issues with the polymers and the temperature they can withstand. Previous studies on the ENose based on polymer-carbon sensor arrays have mainly been performed at constant temperatures [1-5, 9-13].

We undertook an investigation to determine whether using temperature control on the sensors could improve either the identification of analytes with very similar array fingerprints or the identification of mixtures. Eight types of polymer carbon-black composite sensors were tested for their responses to varying analytes at different sensor temperatures. Sensor response was investigated for methanol (10-100ppm), water (7.5-150 ppm) and methane (1,000-16,000 ppm) in the temperature range 28-36°C. We undertook this investigation to determine whether using temperature control on the sensors could provide additional sensor information to improve either the identification of analytes with very similar array fingerprints or the identification of the components in a mixture.

EXPERIMENTAL

Materials

For these experiments, we tested sensors made from six different polymers: Poly N-vinyl pyrrolidone (PVPyr), Poly 2-vinyl pyridine (P2VPy), Poly methyl vinyl ether–alt–maleic acid (PMVe-MA2), Poly 4-vinyl phenol –co – 2 – hydroxyethylmethacrylate (P4VPhcHEMA), ethyl cellulose (EC), and polyvinylidene chloride-acrylonitrile (N). The Poly N-vinyl pyrrolidone (MW = 360,000), Poly 2-vinyl pyridine (MW = 200,000), and ethyl cellulose (48% ethoxyl content) were purchased from Scientific Polymer Products, Inc. The Poly methyl vinyl ether–alt–maleic acid (MW = 216,000) and Poly 4-vinyl phenol–co–

2– hydroxyethylmethacrylate were purchased from Aldrich. The polyvinylidene chloride-acrylonitrile was purchased from PolySciences, Inc. The carbon black used for the composite films was Black Pearls 2000, a furnace black made by the Cabot Corporation. Polymers and carbon black were used as received.

The 2-propanol and 1,3-dioxolane, used to dissolve the polymers and disperse the carbon black, were reagent grade solvents from J. T. Baker and Aldrich, respectively, and were used as received. The water used as an analyte for sensor testing was distilled water. The methanol used as an analyte for sensor testing was reagent grade from Aldrich. The methane was from SoCal Airgas.

Gas Handling System (Analyte Delivery)
For these experiments, to deliver clean air as well as analytes to the sensors for testing, we used a gas handling system built in our laboratory. A more detailed description can be found elsewhere [5]. The gas handling system is run on house air that is filtered to clean and dehumidify it. The flow of the air is controlled by a series of mass flow controllers, valves, and check valves. The air delivered to the sensors can then be humidity controlled: a fraction of the air is bubbled through water and remixed with dry air. All of these experiments were performed using dry air. For methanol and water, a small fraction of clean air is bubbled through the solvent and mixed with the clean air. The analyte concentrations are calculated using the temperature of the air above the bubbler (to determine solvent partial pressure) and the total pressure of the bubbler. For methane, the gas is connecting directly to one of the mass flow controllers and then mixed with clean air. Calibrations of the system are done using a total carbon analyzer, and checked with a GC-MS. The entire system is computer controlled using a LabVIEW program.

Sensors
These polymer-carbon-black sensing films are made by dissolving the polymer in a solvent (~1.0% wt.) and dispersing the carbon black in the polymer solution, 20%, by weight, of carbon black to polymer. For this study, PVPyr, P2VPy, PMVe-MA2 and P4VPhcHEMA were dissolved in 2-propanol. In addition, solutions of PVPyr, P2VPy, EC and N were made using 1,3-dioxolane as the solvent, with 15% by weight of carbon black to polymer.

The sensing films were deposited, or cast, on ceramic substrates; each substrate has eight Au-Pd electrode sets. The sensor substrate is 25 mm x 10 mm; each sensing film covered an electrode set with an area of 2mm x 1 mm. Two polymers were cast on each substrate for a total of four sensors per polymer. The sensor substrate is heated using resistive heaters embedded in the substrate, and the temperature feedback loop is closed using a thermistor that is surface mounted on the back of the substrate. The temperature of the substrates was also monitored using T-type thermocouples mounted on the back of the substrate. Our testing chamber and device electronics can test four

substrates concurrently, for a total of 32 sensors. More detailed descriptions of the sensor chip and device operation can be found elsewhere [1-4].

Sensor Testing
The sensors were placed in our test chamber and were exposed, alternately, to clean dry air and air containing an analyte. For the purposes of these experiments, clean dry air is house air that has been cleaned and dehumidified using filters and contains less than 100ppm of water at 22 °C. For each analyte, five concentrations were selected, and 5-10 measurements at each concentration were taken. The sensor exposures alternate between 60 minutes of clean air and 15 minutes of an analyte concentration. The same exposure sequences were repeated at 28, 32 and 36°C.

Sensor data is measured as resistance versus time and the data is plotted as the normalized change in resistance, $\Delta R/R_0$, where ΔR is (R_t-R_0), R_0 is the resistance at the start of an experiment and R_t is the resistance at time t. Figure 1 shows the response of one sensor to methanol at two different sensor temperatures (28 °C and 36°C). The raw data have been processed using algorithms and procedures developed for the JPL ENose [1-4]; the data have been processed with a background subtraction to correct for baseline drift and then smoothed with a 5-point-average.
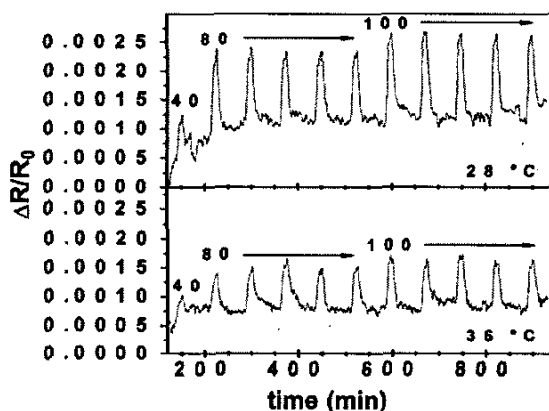

Figure 1. Response of Poly N-vinyl pyrrolidone sensor (1,3-dioxolane, 15% carbon black) to 40 ppm, 80 ppm and 100 ppm of methanol at two different sensor temperatures (top: 28 °C, bottom 36 °C).

RESULTS AND DISCUSSION
Figure 1 shows the normalized change in resistance of a Poly N-vinyl pyrrolidone sensor (1,3-dioxolane, 15% carbon black) to 40 ppm, 80 ppm and 100 ppm of methanol at two different sensor temperatures (28 °C and 36°C). The data are plotted on the same scale for comparison. It is clear that the increase in sensor temperature reduces the sensor response. This decrease in sensor response to methanol with increasing sensor temperature was seen for all six polymers. There were two sets of sensors for PVPyr and P2VPy, and in

these experiments the sensors behaved similarly. The decrease in sensor response to methanol was greatest for the Poly N-vinyl pyrrolidone sensors. The polymers are ranked from greatest to least decrease in response to methanol (at 100 ppm): PVPyr, P4VPhcHEMA, PMVe-MA2, EC, P2VPy, and N.

As with methanol, similar results were seen for the response of all six polymers to water. Sensor response for each analyte event is defined as the normalized change in resistance just before the event and during the plateau of the event: $\Delta R_{(e)}/R_0$, where $\Delta R_{(e)}$ is (R_e-R_0), R_0 is the resistance just before the event occurs and R_e is the resistance at the plateau of the event [4, 5]. Figure 2 shows the decrease in sensor response of all four Poly N-vinyl pyrrolidone sensors to 150 ppm of water. The polymers are ranked from greatest to least decrease in response to water (at 70 ppm): PVPyr, PMVe-MA2, P4VPhcHEMA, P2VPy, N, and EC.
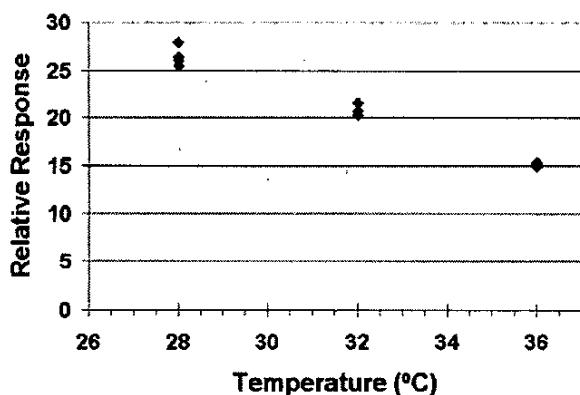
Figure 2. Decreasing Poly N-vinyl pyrrolidone (1,3-dioxolane, 15 wt.% carbon) sensor response to 150 ppm water (5 exposures) at different sensor temperatures. Relative response is $\Delta R_{(e)}/R_0*10,000$.

Similar to the methanol and water, four types of the polymer sensors showed a decrease in sensor response to methane with increasing sensor temperature. Neither the EC nor the N sensors had a reproducibly measurable sensor response for methane at any temperature. For the remaining four types of polymer sensors, at 28°C, all of the sensors saturate in their response above 5000 ppm of methane. Figure 3 shows the average relative response of the four poly N-vinyl pyrrolidone sensors to methane at three different sensor temperatures. At both 28°C and 32°C the sensor response saturates above 5000 ppm. When the sensors are held at 36°C, the sensors show a linear response to methane over the entire concentration range. The P2VPy sensors also went from a saturated sensor response above 5000 ppm at the lower temperatures to a linear response to concentration at the highest sensor temperature. The P4VPhcHEMA and PMVe-MA2 sensor responses were saturated above 5000 ppm at all three temperatures. The polymers are ranked from greatest to least decrease in response to methane (at 6000 ppm): PMVe-MA2, P2VPy, PVPyr, P4VPhcHEMA, EC, and N.
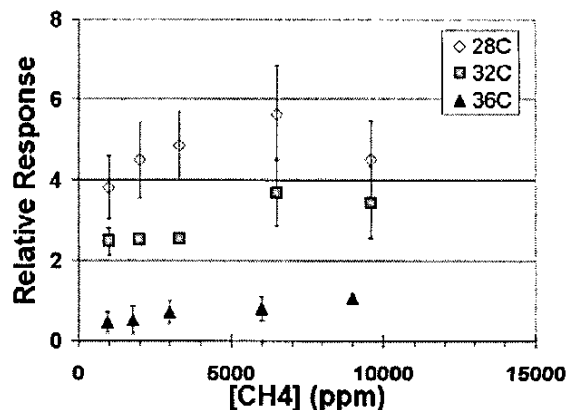
Figure 3. Relative response of Poly N-vinyl pyrrolidone (1,3-dioxolane, 15 wt.% carbon) sensor to methane at different sensor temperatures. Relative response is $\Delta R_{(e)}/R_0*10,000$.

An array response of the eight polymer carbon-black composite sensors was generated from these results for its response to varying analytes at different sensor temperatures. Figure 4 shows the temperature-dependent fingerprints of the polymer-carbon composite sensor array to water and methanol. There are many similarities among the three water fingerprints; e.g., the ranking of the magnitudes of sensor responses does not vary much with temperature: s5>s3>s1>s4>s2>s7>s6>s8. However, within the three water fingerprints, the relative responses of the sensors to each other do change: e.g., the ratio of s5:s3 changes from ~1.3 at 28°C to 1 at 36°C. These data lead us to conclude that analytes can be distinguished based on how the response of the array changes as temperature changes.
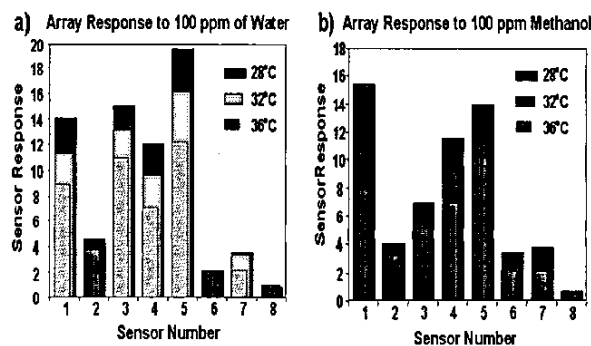
Figure 4. The pattern of response across the 8-sensor array changes as the temperature of the sensor is changed. a) 100 ppm of water b) 100 ppm of Methanol. Sensors: 1: PVPyr (2-propanol), 2: P2VPy - (2-propanol) 3: PMVe-MA2, 4: P4VPhcHEMA, 5:PVPyr (dioxolane), 6: P2VPy (dioxolane), 7: EC, 8: N

CONCLUSION

While all the polymer sensors show a characteristic decrease in sensor response with increasing sensor

temperature for each exposure to the analytes, the decreases are dependent on both the polymer and the analyte. In effect, two sensors of the same polymer at two different temperatures function as different sensors (albeit similar). If no new information is obtained from the temperature measurements then the additional measurements will only increase the complexity of the identification and quantification algorithms for the array. In cases where it is desirable to identify new analytes using a previously selected and trained array, it may be possible to resolve analytes with similar patterns by measuring the sensors responses at two temperatures. In the case of methane, it is clear that measuring sensor response at two temperatures will also help improve quantification of the analyte. Future work will include experiments on both a broader selection of sensors and analytes, as well as testing of the data with the current identification and quantification algorithms.

ACKNOWLEDGMENTS

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